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LASER INDUCED STRUCTURAL CHANGES IN POROUS GLASS DUE TO HOT AND COLD COMPACTION

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A comparison is presented of the structural changes occurring in porous glass during laser-induced hot and cold compaction. The changes occurring in modified regions of different compaction processes when a porous-glass plate with a micro-region is sintered in a furnace are also compared.

Key words: porous glass, low-intensity laser irradiation, weak absorption of radiation, hot compaction, cold compaction.

In recent years a great deal of attention has been devoted to the formation of modified regions (MR) of different sizes and shapes on the surface and in the interior of optically transparent materials as well as to the formation of 3D microstructures of arbitrary complexity, openings and channels, comprising the basis of photonic devices widely used in integrated optics and laser engineering. Laser microprocessing for the formation of such MR has undergone intensive development [1, 2]. Such development was possible because of the relative simplicity and high workability of laser methods as compared with, for example, those based on photolithography. Work is now being done on the formation of MR using different materials, such as glass with complex composition, including doped with transition metals [3], fused quartz [4] and other high-silica compounds, such as porous glasses (PG), which are products of through chemical etching of two-phase alkali-borosilicate glass [5, Chap. 10], and quartzoid glasses (QG) [6], obtained when PG are sintered in a furnace [1].

Near-IR and visible-range ($\lambda < 800$ nm) femtosecond lasers are usually used as the radiation source for forming MR with all of the shapes mentioned [2]. As a rule, $10.6\ \mu\text{m}$ cw CO₂ lasers [1, 7] and UV-range ($\lambda > 250$ nm) lasers [8], whose radiation lies in the fundamental absorption range of glass, are used to form MR on a PG surface.

Porous glasses possess a number of properties including the following: transparency in the visible range; optical strength combined with regulatable nano-range pore sizes; thermal, chemical and microbiological stability; stable properties during prolonged operation; and, unique adsorption properties [9]. All this makes PG promising materials for creating MR on a surface and in the interior.

Local modifications of PG structure which are based on heating by laser radiation are presented in [1], where cw and pulsed CO₂ lasers ($\lambda = 10.6\ \mu\text{m}$) were used as sources of laser radiation. The heating of PG due to the absorption of laser radiation within the interaction region results in hot compaction, i.e., transformation into quartzoid and, correspondingly, the formation of a quartzoid MR. Such a MR surrounds a so-called transitional layer, whose porosity varies evenly from zero in the MR to that of the PG plate [10, 11]. The dimensions and shape of the thermally compacted region can be set by changing the parameters of the laser radiation (intensity, focusing spot size, scan rate during ruling).

Hot compaction by laser radiation is local and differs from furnace sintering [12] by the fact that the heating of PG is limited to approximately the cross section of the beam; it starts at the surface, and then the hot-compaction boundary advances into the interior of the sample [10, pp. 8 – 15]. The change occurring in the porous structure under hot compaction by laser radiation is essentially identical to furnace sintering and occurs at the same temperatures [10, pp. 18 – 20].

One drawback of PG is that such glass ages during long-term storage in air [13]. This process is related to, above all, the presence of fine silica inside the pores in the glass and

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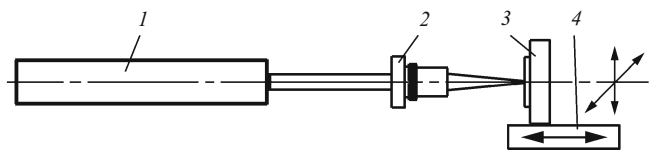


Fig. 1. Scheme of the experimental setup: 1) laser module; 2) LOMO microscope objective 10 \times /0.25; 3) PG sample; 4) coordinate table.

manifests in decreasing specific surface area as the pore radii increase. In time such a structural change results in a change of the sorption and optical (transmission) properties of the PG. To preserve the properties of the MR, above all, the optical properties, it is proposed in [11] that a PG plate with a MR be sintered in a furnace up to the transformation of the PG plate into a quartzoid. It is also shown that the quartzoid region — a MR formed with rapid by laser radiation and rapid cooling — can be preserved by sintering the PG, and in addition the conditions under which a MR can be preserved are determined.

The preservation of a MR by furnace sintering a plate with such a region, i.e., by transforming a PG plate into a quartzoid, opens completely new prospects for using planar MR of this kind. It is obvious that despite all its attractions (speed of operation, repeatability of the results, locality) this method cannot be used to form MR in the interior of a plate, the need for such regions increasing year after year. For this reason, for a long time repeated attempts were made to develop a method for forming MR locally in the interior of a PG-based plate.

In order to form a MR in the interior of a plate the plate's material must be transparent to the laser radiation. But then the formation of a MR must be based not on a thermal but rather a different effect and the process where the characteristics of such a non-thermal MR are preserved by furnace sintering the plate with the MR must also be different.

A method, called cold compaction, of forming a MR locally in the interior of PG by laser radiation which is weakly absorbed by the PG plate but nonetheless results in compaction within the irradiation zone was proposed recently [14]. It is obvious that a universal operation of furnace sintering the PG plate will have to be used in order to preserve the characteristics of such MR during long-term storage and operation. In this case the process of preserving the MR by sintering a plate with a MR will be very different.

The objective of this present work is to compare the structural changes occurring in PG as a result of hot and cold compaction by laser radiation as well as the changes occurring in the MR when the plate with the MR is furnace sintered.

Experimental Part. Non-porous silicate glasses with the following composition were used for cold compaction (wt.%): 94.73 SiO₂ – 4.97 B₂O₃ – 0.30 Na₂O with possible traces of Al₂O₃ ($\leq 0.1\%$). The MR in the interior of the PG

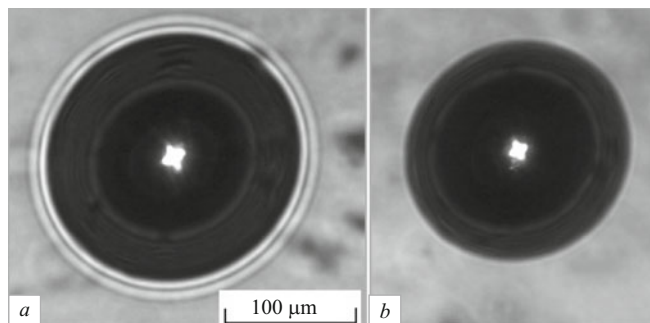


Fig. 2. Photographs of a microsphere formed by cold compaction, in transmitted light before (a) and after (b) sintering.

were formed by linearly polarized cw laser radiation with wavelength $\lambda = 808$ nm and optical power $P = 120$ mW. The absorption coefficient for the incident radiation was $\alpha \approx 0.0067$, i.e., the PG sample can be regarded as transparent for this wavelength. The radiation from the laser 1 was focused by means of a microscope objective 2 onto the sample — the PG plate 3, which was secured on a coordinate table 4 (Fig. 1).

The formation of the MR in the PG interior started at laser irradiation time $t \approx 300$ sec. The spot size on the surface of the plate was $d = 50$ μ m. The size of the beam focused into the interior of the glass was $d_0 \approx 25$ μ m, the power density in the focusing plane $q \approx 2.45 \times 10^4$ W/cm², and the energy density $\varepsilon \approx 7.34 \times 10^6$ J/cm². A view of the spherical region is shown in Fig. 2. It is evident that on the basis of its shape the region formed is reminiscent of a sphere with diameter $d_{sp} = 185$ μ m. A brighter region with diameter at the center $d_{c,r} = 114$ μ m can be seen inside this region.

An Axio Imager A1m Carl Zeiss microscope was used to study the MR, obtained in the glass interior, in transmitted and polarized light with magnification $\times 100 - \times 200$.

Results and Discussion. Experimental data on thermally compacted regions — MR, formed by CO₂-laser radiation on the surface of PG plates, and the experimental data on the size change of the MR and the PG plates during sintering are presented in [11] (Fig. 3). It is shown that for sintering time 10 – 15 min the MR increases in size as a result of sintering of a transitional layer, while the dimensions of the PG plate decrease because of shrinkage due to the closure of pores and channels in the GR. The shrinkage of the PG plate is accompanied by a gradual increase of the density of the glass before it transformed into a quartzoid. For sintering time 15 – 25 min no changes occur in the plate size while the MR continues to increase in size slowly. The MR–quartzoid boundary becomes sharper. The sharpness of the MR–quartzoid boundary continues to increase for sintering time 25 – 35 min. For sintering time longer than 35 – 40 min the density of the MR becomes the same as that of the quartzoid plate, as is evidenced by the partial vanishing of the MR–quartzoid plate boundary.

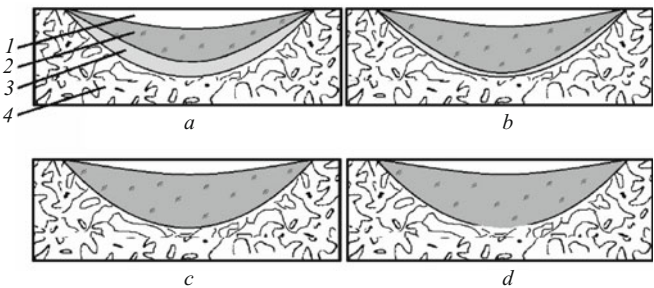


Fig. 3. Schematic image of a hot-compacted region formed on a PG sample by CO₂-laser radiation: 1) region of shrinkage; 2) hot-compaction zone; 3) transitional layer; 4) PG plate; a) formation of a hot-compacted region in 10 – 15 min; b) 15 – 25 min; c) 25 – 35 min; d) > 35 – 40 min.

The local change in density and therefore refractive index due to cold compaction of PG is based on mass transfer from the edge of the interaction zone toward its central region. The reason for such transfer is still not clear but studies of the complex structure of a microsphere (Fig. 4), formed within the laser irradiation zone on weakly absorbing PG, indicate a local radiation-induced change of PG density. The MR formed consists of a central region, whose channels are almost completely filled with matter transferred from the edge layer. In turn the channels in the edge region are largely free of matter. Investigations of the complex structure of the microsphere performed by polarization interferometry and by methods based on measuring the transmission and reflection spectra of the different parts of the microsphere show unequivocally that the refractive index in the central region is close to that of the quartzoid while the refractive index of the edge layer is lower than that of the PG plate.

The parts of a microsphere formed in this manner retain their dimensions for a long time. The transmission of the PG plate decreases as a result of its layered structure, which in turn changes the optical properties of the MR. For this reason, a universal sintering operation must be used in this case in order to stabilize the optical characteristics of both the PG and MR. For MR with a complex structure, the sintering process required to stabilize the optical properties of the MR and PG plate containing this MR is conducted for 10 min at temperature 870°C, which ensures that the PG plate is converted into quartzoid. It has been determined that such a transformation is accompanied by a volume decrease, i.e., shrinkage of the microsphere as a whole equal to the pore volume in the

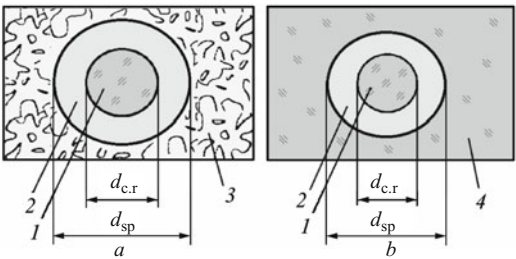


Fig. 4. Schematic image of the MR with cold compaction in the PG interior before (a) and after (b) sintering: 1) central region; 2) edge layer; 3) PG plate; 4) quartzoid plate; $d_{c,r}$) diameter of central region; d_{sp}) diameter of sphere.

microsphere, and a different change of the volumes of each part of the microsphere, which indirectly confirms that the assumption of mass transfer from the edge layer into the central region is correct. Measurements of the volumes of the microsphere and its parts before and after sintering (see Table 1) showed that the shrinkage of the central region of the microsphere is almost three times smaller than that of the edge layer. The size of the MR was measured to within 1.56%.

It is obvious on this basis that the complex structure of the microsphere also remains when the PG plate with the MR is sintered in a furnace. Once again the MR consists of a central region whose index of refraction is practically equal to that of the quartzoid plate and an edge layer whose refractive index is apparently even lower than that of the initial PG.

Conclusion. The formation of MR, regions where the density is higher than that of the surrounding PG plate, is based on different phenomena — hot compaction as a result of laser radiation absorption within the irradiation zone and mass transfer from one part of this zone (the edge layer) into the central region driven by the laser radiation to which the PG plate is transparent. Even though the MR can form by different methods the result of laser radiation is the same.

The purpose of furnace sintering PG plates with MR is to stabilize their long-time optical properties. In both cases the shape of the MR is preserved but in the case of hot-compacted MR sintering increases the MR volume and decreases the shrinkage zone, while in the case of MR formed by cold compaction sintering reduces the volume of the microsphere as a whole and reduces the volumes of its parts by different amounts.

TABLE 1. Size of a MR and Its Different Parts

Period	MR diameter, μm		MR volume, μm^3		
	entire region	central part	entire region	central part	edge part
Pre-sintering	185 ± 2.89	114 ± 1.78	3.314×10^6	0.775×10^6	2.538×10^6
Post-sintering	168 ± 2.62	110 ± 1.72	2.481×10^6	0.697×10^6	1.785×10^6
Post-sintering shrinkage of region			0.749	0.898	0.703

For MR formed on the basis of mass transfer and cold compaction the complex structure of the MR is also preserved. Scattering of optical radiation could become a basic application of MR with such a structure. It will be possible to view MR of a cold-compaction region in the form of bands, whose size decreases correspondingly from 30 – 120 to 5 – 10 μm , as volume waveguides.

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